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*THE INTERNAL RESISTANCE OF THE LEAD
ACCUMULATOR.*

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GENERAL DISCUSSION.

1. THE internal resistance of a lead accumulator is not a factor of importance in the practical operation of storage batteries. In a small pocket battery it is only a few hundredths of an ohm: in medium sized cells it sinks to a few thousandths, and in large cells, such as are used in regulation and central station work, it is of the order of a few hundred-thousandths of an ohm. In almost every case the cell resistance is so low in comparison with the other resistances in the working circuit that it can be neglected as far as practical calculation is concerned.

But the resistance of a cell and the changes which take place in this factor are of much interest when the behavior of the cell is being studied from a more general point of view. A lead accumulator seems a very simple system indeed at first glance, but it is in fact a very complex one, concealing many problems difficult of solution. While the cell is at rest, fully charged, and therefore containing plates which are good conductors from their center out to the boundary of the electrolyte, its resistance is very nearly that of the acid between these plates, and it can be calculated with fair approximation. But when the cell is working, either on charge or discharge, its condition is most variable. The acid must diffuse through a series of fine channels, and great differences of acid concentration in the different layers of the plates will be set up. Then, too, the particles of lead and lead peroxide, themselves good conductors, will be more or less completely coated with lead sulphate—a bad conductor. The acid concentration will, moreover, be a function of the *rate* at which the cell is working, and the thickness of the lead sulphate coating over a particle of lead or lead peroxide at any given point in the plate will also be a function of the rate.

2. An ideal section of a storage battery of two plates is shown in

Figure 1. *A* is the plate, and its resistance can be assumed to remain fairly constant, except for its temperature coefficient. This factor has a small value within the range of practical operating conditions. *C* is that part of the electrolyte which does not lie very close to the plates. Its total concentration is determined accurately by Faraday's Law and its resistance is a function only of this concentration and of the temperature. *B* is the most active, variable, and interesting part of the cell. It includes the active material, that part of the electrolyte which is in the pores of this material, and that part of the electrolyte which is

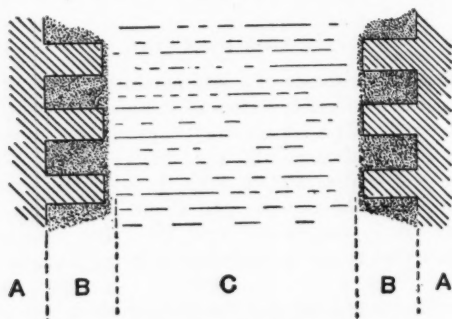


FIGURE 1. Section through storage cell.

near the plates. For ordinary rates large concentration changes can be assumed to extend not more than a millimeter or two from the outside surface of the active material before they are equalized by mixture with the main body of the electrolyte.

When the cell is at rest, its resistance may be considered as being made up of three parts. *A*, metallic in nature, and therefore with a negative temperature coefficient, but constant at a fixed temperature. *B*, also metallic in its nature, and sufficiently low so that the resistance of the electrolyte in its pores can be neglected in comparison with it. *C*, a purely electrolytic resistance, with positive temperature coefficient, but constant at a fixed temperature.

When the cell is working at a constant rate and fixed temperature, *A* remains constant. *C* is a function only of the total concentration of acid in the cell, and can be made constant by using small plates and a large body of electrolyte. The resistance of *B* now becomes more complex, and may be considered to break up into two parts, one a function of the condition of the active material and the other a function of the

concentration of the electrolyte in the pores of the active material and in the layer in immediate contact with its surface.

The change in B during charge will, moreover, be wholly different from the change during discharge, for in both cases the changes in the active material *follow the electrolyte*. During charge the active material first to enter into reaction is that at the surface of the plate, provided the plate has not been allowed to "sulphate" so completely that the conductivity through the active mass has been very greatly reduced. Since the action is taking place at the surface the electrolyte does not have to diffuse far through narrow channels. But as the diffusion path increases and the cell becomes more fully charged, concentrated acid is produced in the pores of the mass. In spite of the decrease in resistance due to this better conducting acid it is still the plate itself which does most of the conducting. It is therefore to be expected that the change of resistance during the charge of a healthy storage cell will not be large.

During discharge a very different state of affairs exists. In this case also action begins at the surface of the plate, where electrolyte is available for the reaction. But as discharge proceeds, and the area of activity recedes into the interior of the active material, acid is used up within the plate and the concentration of the active part of the electrolyte decreases. To this loss is added the loss of conductivity of the plate itself, for the particles of lead and lead peroxide in the outer layers have now been covered with sulphate and more or less completely insulated from each other. The result is as if the distance between the plates had been increased, for the plate surface which is actually carrying current is now well back in the interior of the mass of active material, instead of at the actual outside surface.

It should be kept in mind also that the equalization of concentration differences in a working plate is not cared for wholly by diffusion. While this is a potent factor always, it can be shown to be insufficient to account for the facts. A considerable part of the equalization is probably cared for by local concentration cells at various parts of the plate, and these local actions depend for their efficiency on good conductivity of the plate between the points where the concentration differences exist. Any change in the conducting power will affect the rate of equalization of acid and will displace the area of action within the plate.

Viewed in this way we should hardly expect any very large or very rapid changes in cell resistance, nor any of the peculiar maxima of resistance at various points in charge and discharge which appear in some of the older reports on the subject. It is probable that polarization was not eliminated in these measurements.

On long standing, a storage cell may acquire a very high resistance indeed as the result of complete "sulphation." This term means that the active lead sulphate formed during discharge has gradually changed into the crystalline inactive form and that crystals of this form have completely covered the particles of lead and lead peroxide with an insulating coating. Authentic cases of cells of considerable size, with internal resistance as high as 10 ohms, are known. But under the usual conditions of charge and discharge the sulphate retains its "active" state, and even after standing discharged for a month or more no great change in internal resistance is usually to be observed [see § 15].

3. In its ordinary work, a storage cell is discharged only until the plate potential sinks to about 1.7-1.8 volts. This means usually that only about one quarter of the active material in the plates has entered into reaction and that the increased resistance in the active material is due rather to separation of the particles by sulphate coatings than to complete transformation of the active material at any point into insulating material (sulphate). On charge these sulphate coatings and bridges are rapidly broken down, and the decrease in resistance is therefore much more rapid than that corresponding to change in electrolyte within the plate.

After a period of discharge, with corresponding change in resistance, the cell recovers its original e. m. f. along a curve which is somewhat like a diffusion curve [§ 13]. This curve is made steeper by the equalizing effect of local action as explained in 2. It also recovers its original resistance along a somewhat similar curve. These facts indicate clearly the *dynamic* nature of the whole cell activity, for evidently the change in resistance as well as the change in e. m. f. is fundamentally a function of acid concentration and diffusion. The particles of active material cannot have been completely covered by insulating layers, for on standing the plate returned to its original condition as measured by e. m. f. and resistance.

We must evidently think of the particles of lead and lead peroxide as covered with a spongy or powdery layer of lead sulphate, with interstices so small that diffusion cannot overcome the effect of even a small current and its accompanying exhaustion of acid within the pores. As long as no current is flowing, and when recovery has been allowed to take place completely, the total active surface has not been greatly reduced by the changes in the plate, nor has the "active surface" been far removed from its original plane. But the passage of even a small discharge current causes exhaustion of acid in the pores to such an extent that nearly pure water intervenes between the electrolyte

and the conducting material of the plate, and the result is a considerable increase in resistance.

While it is true that the concentration and therefore the resistance of the main body of the electrolyte is completely determined by Faraday's Law, the passage of the same quantity of electricity may result very differently in various types of cells. Change in concentration and resistance will be great in those types which have large weight of plates in proportion to their content of electrolyte. They will be small in the types where weight is not a factor to be considered and where a large excess of acid is maintained.

Other factors which may effect resistance will be discussed in connection with the data of this paper.

4. On page 611 will be found a list of references on the subject of the resistance of galvanic cells and accumulators. Many of these papers were written at a time when the difficulty of such measurements was not understood, and it may be said that the research of Nernst and Haagn (1896) was pioneer work, and that they showed for the first time how to eliminate the disturbing factors of the problem. The measurements of Dolazalek and Gahl (1901) are still more accurate and include data on several types of cell and on various rates of charge and discharge.

Our attention has been turned largely toward the temperature coefficients of resistance under various conditions, for we wished to exhibit as clearly as possible the dynamic nature of the phenomena in the lead accumulator. After investigation of the other methods of measurement, we adopted the form of bridge described by Ayres [20]. Ayres himself did not use the bridge for measurements on storage cells, nor indeed for any very low resistances of electrolytic nature. But we have found this type of bridge, with slight alteration, to be most satisfactory for the measurement of electrolytic resistances of the order of 0.01 to 0.10 ohm.

THE BRIDGE AND AUXILIARY APPARATUS.

5. The bridge connections are shown in Figure 2, together with the circuit used in charging and discharging the cell and the secondary bridge on which resistances were measured after balance had been obtained. The bridge itself is symmetric, and contains a meter slide wire of manganin of about 0.40 ohm resistance. At opposite ends of this wire connection is made to the source of alternating current and to the two other arms of the bridge. The cell arm contains the cell under investigation in series with a capacity C_1 : the other arm con-

tains a similar and nearly equal capacity C_2 and the variable resistance R . C_1 and C_2 are rolled paraffin paper condensers of about 22 microfarads each, composed of 10 units of 2.2 mf. connected in parallel by No. 11 copper wires soldered at each point and also to the bridge connections. The entire wiring of the bridge was non-inductive.

The cell was maintained at constant temperature in a thermostat and was connected by soldered No. 11 wires terminating in a heavy mercury-metal switch-block so arranged that the cell could be placed

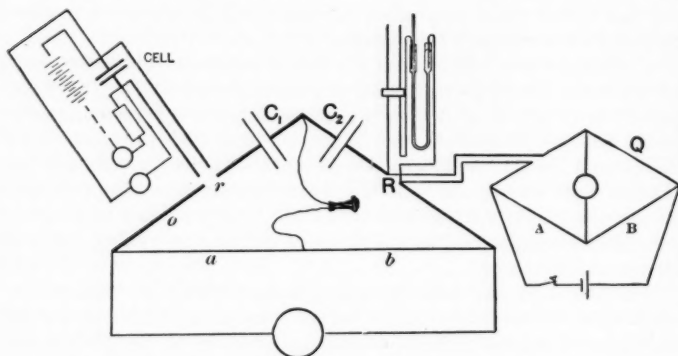


FIGURE 2. Bridge connections for measuring low electrolytic resistances.

in circuit, or cut out, without change in the block resistance and without short-circuiting the cell. The $\frac{1}{4}$ -inch wires of the block switch were kept continually under mercury whichever way the switch was turned, thus keeping contacts bright when the cell was out.

The variable resistance R consisted of two parts: One of two parallel wires shunted by a heavy sliding block, and the other, in series with this, was a vertical U-tube of glass containing mercury, as shown in Figure 3. The connecting wires dip into the mercury in the two arms and the cross-section of one arm was decreased or increased by lowering or raising the glass rod. This smoothly variable resistance proved to be of the greatest aid in obtaining the close settings desired.

In parallel with R was a box Wheatstones bridge and galvanometer. R could be thrown over into the X -arm of this bridge by means of a mercury switch, but as the box bridge had a resistance of about 1000 ohms it was found unnecessary to cut it out while making settings on the cell, and during the later measurements the switch was

removed, leaving the connections as shown in Figure 2. The ratio of the fixed arm of this auxiliary bridge was 1 : 1000 and resistances could be measured on it to 0.0001 ohm.

During the majority of our measurements a resistance of a few tenths of an ohm (O in the figure) was kept in the cell arm in series with C_1 and for some measurements of high resistances it was found necessary to introduce a similar resistance in series with the slide-wire and mercury resistances of R .

Measurements were made with "cell in" and "cell out" within as short a time as possible, in order to eliminate any possible changes, and measurements were repeated several times in each case. We were thus measuring the difference between $[\text{cell} + R_1]$ and R_1 , where R_1 is the resistance of O plus the connections in that arm.

Various sources of alternating current were tried, but none was wholly satisfactory. We had no source of pure sine-waves at our disposal and some trouble from harmonics was experienced. This was removed by using a transformer and various combinations of capacities in the circuit.



FIGURE 3. Variable mercury resistance.

THEORY OF THIS TYPE OF BRIDGE.

6. The complete theory of this type of bridge may be found in Ayres's paper [20], but our method of operation was necessarily somewhat different from his because of the small magnitudes of the resistances we had to measure.

For the ideal condition of balance we have

$$(1) \quad r/R = a/b = C_2/C$$

where the bridge is non-inductive, the resistances of connections are negligible, a and b are the bridge-wire readings, C_2 is the capacity of the "known" arm, C is the resultant of the capacity of the cell with C_1 , r is the resistance of the cell and its leads, and R is that of the opposite arm of the bridge.

Taking into consideration the resistances of the various connections, and that of the coil o inserted in the cell arm, we have, for both bridges, the following equations :

$$(2) \quad \frac{a}{b} = \frac{o + r + u}{R + v},$$

where u and v are the resistances of the connections on the cell side and the R side respectively ;

$$(3) \quad R + w = Q \frac{A}{B} = Q(0.001) = q,$$

where w is the resistance of connection to the auxiliary bridge. Combining (2) and (3) gives

$$(4) \quad o + r = (q - w + v) \frac{a}{b} - u.$$

Upon cutting out the cell and short circuiting that arm of the bridge, we have

$$(5) \quad o = \left(Q' \frac{A}{B} - w + v \right) \frac{a'}{b'} - u = (q' - w + v) \frac{a'}{b'} - u.$$

Subtracting (5) from (4) gives

$$(6) \quad r = \frac{a}{b} \left(q - q' \frac{a'b}{ab'} \right) + \frac{a}{b} \left(\frac{a'b}{ab'} - 1 \right) w - \frac{a}{b} \left(\frac{a'b}{ab'} - 1 \right) v.$$

During the first part of the investigation a lay between the limits 506 mm. and 507 mm., and during the second part between 481 mm. and 486 mm. In most cases the difference between a and a' was less than 0.5 mm., and it was usually about 0.3 mm.

In view of this, the terms containing w and v can at once be neglected. The difference between $q - q'$, the value actually recorded as resistance, and $(q - q') \frac{a'b}{ab'}$, is $\left(\frac{a'b}{ab'} - 1 \right) q'$, which does not exceed 0.0005 ohm, since q' did not exceed 0.25 and the value of the parenthesis was in no case greater than 0.002.

The following observations are deemed interesting in connection with the fact that the bridge reading was not the same with the cell in as when the cell was out.

1. The bridge reading with "cell in" a is smaller than a' .
2. Both with "cell in" and "cell out," the insertion of a condenser (5.2 MF) in parallel with the leads to the cell-switch causes an increase in the value of a or a' as the case may be.
3. Decreasing the frequency by 50% causes no change in a , but a' is thereby decreased.
4. A condenser in parallel with C_1 causes a and a' to decrease.

The last observation is to be expected from the theory of the bridge. It is hard to see how any capacity possessed by the cell could act so as to make a smaller than a' ; rather the opposite effect would be ex-

pected. The supposition of an inductance in the cell would explain this change in the bridge reading, but a change in the frequency did not affect a , while it did affect a' .

The explanation would seem to be as follows: The configuration of R suggests inductance, and an approximate calculation shows $2\pi nL_2$ to be about 0.01. Now the value of $1/2\pi nC_2$ is about 5. A change of 0.5 mm. from a to a' corresponds to a change of 0.01 in $1/2\pi nC_2$. Calculation gives about 0.01 for $2\pi nL$ for the leads from the cell-switch to the cell, corresponding to $2\pi nL_2$ for the C_2 arm of the bridge. From these considerations it would appear that a rather than a' is more nearly the point where $C_2/C = a/b$, for, with "cell in," the inductive reactance of the C_2 arm is balanced by that of the cell leads.

Since C_1 and C_2 are about the same, and since C_2 has an inductance with it, while C_1 has not, the reactance of the C_2 arm will increase with decrease of frequency faster than the reactance of the C_1 arm; in short, the reactance of the C_2 arm will become greater than that of the C_1 arm, and a' will diminish with decrease in frequency. On the other hand, with "cell in," the two reactances will change equally with change in frequency, that is, a will not change.

7. From the average of all our measurements we have compiled the values for the open circuit resistance of our cell at various temperatures. They are as follows:

TABLE I.

OPEN CIRCUIT RESISTANCE OF PLANTÉ PLATES AT VARIOUS TEMPERATURES.

Temperature.	Resistance.	Temperature.	Resistance.
0.0 C°	0.0686	25.0	0.0448
8.5	0.0579	30.0	0.0420
10.0	0.0562	45.0	0.0362
20.0	0.0483	55.0	0.0335

These values are plotted in the full-line curve of Figure 4. In the dotted-line curve on the same figure are given the values for sulphuric acid of the same concentration as that used in our cell. We have chosen the two points indicated by larger circles as the points from which to calculate the remainder of the curve, which is plotted from the empirical formula

$$K_t = K_0 (1 + ct + c^2t^2)$$

It will be seen that the cell resistance and the acid resistance fall very closely together from zero to 30°. Above this point the cell re-

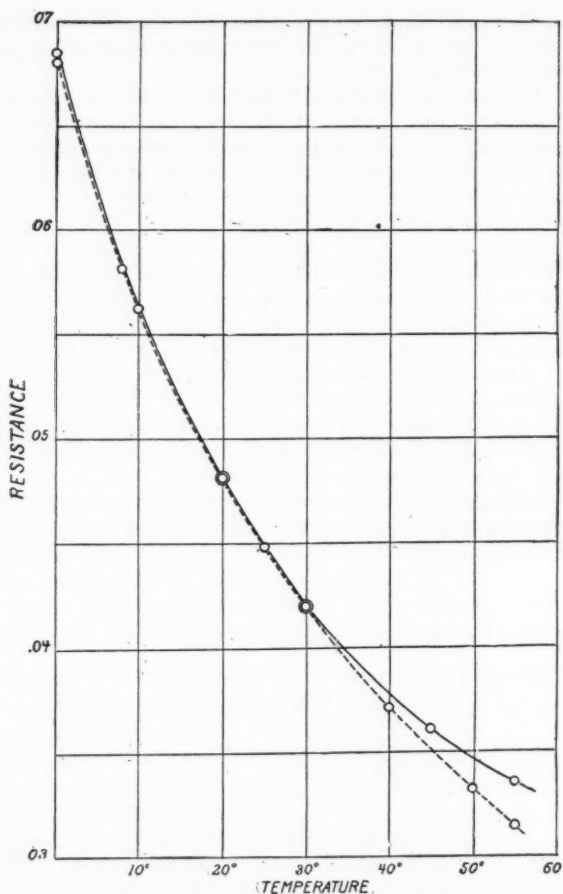


FIGURE 4. Temperature-resistance curves for electrolyte and cell.

sistance does not decrease as rapidly with rise of temperature as does the acid. As a matter of fact the two points at zero do not fall together. So it is evident that both at high and low temperatures the cell resistance is higher than that calculated for the pure acid. This figure indicates merely the shape of the two curves with reference to

each other, and by no means indicates that the resistance of the cell is the same as that of sulphuric acid of the same concentration between a pair of platinum electrodes placed in the same geometrical position as the "average plate surfaces." The plate resistance is not negligible and its negative temperature coefficient may account for the higher resistance at the higher temperature in part at least. That the resistance of the plate itself enters is clearly shown by the fact the pasted

TABLE II.

INTERNAL RESISTANCE OF A PLANTÉ CELL DURING DISCHARGE
AT 2 AMPERES. TEMPERATURE 8.5° C.

Time.	Cell in.	Cell out.	Cell.	Voltage.
0	.2882	.2304	.0578	{ 2.09 open-circuit 1.85 after closing
10	.2895	.2317	.0578	1.83
22	.2926	.2306	.0620	1.77
37	.2961	.2316	.0645	1.70
52	.3080	.2313	.0767	1.55
62	.3142	.2316	.0836	1.36
71	.3158	.2315	.0843	1.18
77	.3160	.2316	.0844	0.97
81	.3164	.2315	.0849	0.80
86	.3191	.2314	.0877	0.63
96	.3656	.2315	.1341	0.30 [reversed]

plates of slightly greater area, placed as nearly as possible the same distance apart, show a decidedly greater resistance on open circuit than that of these Planté plates, which have a solid lead web and lead ribs running their whole length. The cells with pasted plates have nearly .01 ohm more resistance.

8. The values of Table 2 are plotted in the upper curve of Figure 5, and they show the characteristic course of changes in this particular type of plate. The cell changes its internal resistance a little more than 100 percent during complete discharge, and by the time the last value on the list is reached the cell voltage has dropped to zero.

The most interesting thing about the curve is the flat place which occurs after 60–80 minutes of discharge. This is quite characteristic of Planté plates with ribs, but it has never been noticed before by any of the observers who have worked on storage cells. Indication of such a flat place may be seen in some of Haagn's curves, but it would seem that he thought them due to errors of measurement.

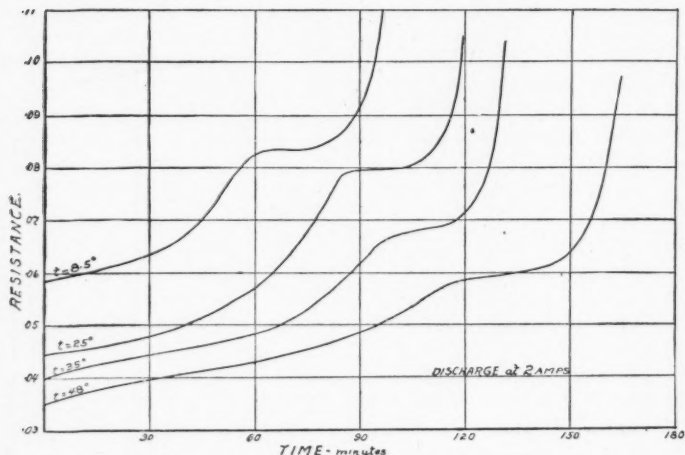


FIGURE 5. Curves of resistance of Planté cell during discharge at various temperatures.

The reason for the appearance of such a change in curvature seems quite obvious. These plates are of the Gould type, and they have ribs spun from the lead of the originally flat plate. These ribs are changed by formation to form active material, which lies close to the ribs at their tops but which forms a solid mass down toward the center web of the plate. During the first part of the discharge the electrolyte finds active material on the ribs and diffuses largely into the almost open space between them. As this material is used up the action moves further into the plate and presently reaches the mass of material which fills the bottom of the grooves. Here for a time there is material enough at a practically constant distance from the surface of the plate to supply the action, and when this is used up the resistance rises very rapidly and the plate potential shows that the cell is completely discharged.

TABLE III.
PLANTÉ CELL. DISCHARGED AT 2 AMPERES.

Temperature 25° C.					
Time.	Cell.	Voltage.	Time.	Cell.	Voltage.
Open circuit	.0448	..	76	.0690	1.62
0	.0448	..	92	.0796	1.43
8	.0453	1.89	103	.0800	1.28
15	.0472	1.88	110	.0823	1.16
32	.0481	..	120	.1061	0.26
48	.0527	1.78	126	.1365	0.00
62	.0570	1.70			
Temperature 35° C.					
Open circuit	.0400	..	94	.0650	1.57
8	.0399	1.92	105	.0678	1.42
19	.0430	1.91	110	.0682	1.38
33	.0452	1.87	121	.0720	1.25
49	.0465	1.84	127	.0800	0.65
67	.0492	1.77	134	.1300	0.30
82	.0579	1.70	147	.1901	0.00
Temperature 48° C.					
Open circuit	.0351	..	112	.0570	1.65
6	.0358	1.96	120	.0589	1.57
23	.0395	1.95	131	.0598	1.52
37	.0406	1.90	136	.0600	1.47
46	.0420	1.87	144	.0620	1.37
63	.0431	1.84	153	.0653	1.00
79	.0460	1.80	159	.0945	0.52
92	.0488	1.76	173	.1757	0.12
103	.0520	1.70	178	..	0.00

As will be seen later, paste plates show no such flat place in their curves. [§ 11.]

The values for this Planté cell, discharged at 2 amperes at various temperatures [Table III], are all plotted on the curves of Figure 5. The corresponding voltage curves will be found in Figure 6.

The characteristic points appear in each curve, and the flat place moves toward a later point in the discharge curve, as might be ex-

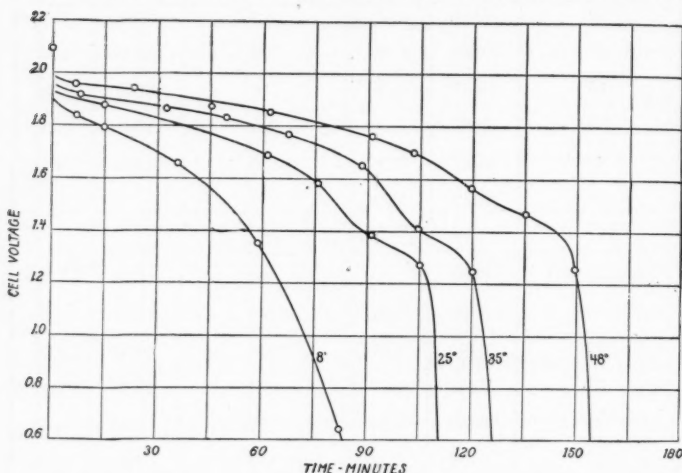


FIGURE 6. Voltage curves of Planté cell during discharge at various temperatures.

pected, when the temperature is raised. This means merely that the material of the plate can be better reached and utilized at the higher temperature, and that therefore more of the active material on the ribs enters the reaction, leaving the mass of material at the bottom of the grooves for a later period of the discharge.

It is by no means easy to be sure that the cell has reached the steady state corresponding to any given temperature, except by maintaining it at the new temperature for several hours. The lag of resistance behind its final value when temperature is quickly changed is very noticeable and caused us much trouble. We finally found it best to keep the cell for at least six hours at the new temperature before trying to take a discharge curve.

It will be noticed that the curve for 25° C. does not fit in very well

with the rest of the set. Most of our measurements at this temperature were made at the beginning of the work, and it is quite possible that some lag error has caused this slight variation. The values for resistances at 8.5° were still harder to fix, but the curve given is the average of so many measurements that its correctness is fairly certain. At the higher temperatures the lag becomes much less troublesome. The explanation which suggests itself is that this slow change corresponds

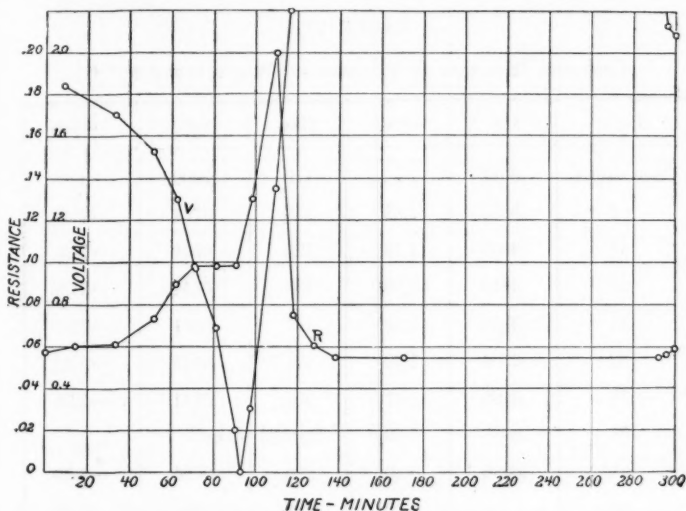


FIGURE 7. Resistance and voltage curves for a Planté cell during complete discharge and reversal.

to a chemical reaction. Probably lead sulphate is dissolved as the temperature is raised and precipitated as it is lowered. This would be just such a process as would result in the slow adjustment of the cell resistance to a new temperature.

This explanation is made more probable by some experiments we have made in an ordinary conductivity vessel with platinum electrodes, filled with sulphuric acid from our cell. Some pieces of lead and lead peroxide from a partially discharged cell were placed in the vessel and the conductivity followed after a change in temperature. The lag of resistance behind temperature is just as noticeable in this arrangement as in the more complicated cell under investigation, and there seems to

be no doubt that the explanation given is the correct one. A similar lag in the e. m. f. following a change in temperature is to be expected, and this has been noticed by Dolazalek during careful determination of the temperature coefficient of the e. m. f. of a lead storage cell.

The curves of cell voltage during discharge are given in Figure 6, and the flat place in the curve is evident in all except the curve for 8.5°. It is possible that we missed it in this case by not taking points

TABLE VI.
COMPLETE REVERSAL AT 2 AMPERES. TEMPERATURE 8.5° C.

Time.	Cell.	Voltage.	Time.	Cell.	Voltage.
Open circuit	.0577	. . .	110	.2000	-1.36
8	.0585	1.83	118	.0751	-2.30
14	.0600	1.78	128	.0604	-2.33
33	.0610	1.70	138	.0554	-2.35
51	.0739	1.53	147	.0571	-2.37
62	.0904	1.30	171	.0545	-2.44
71	.0980	0.97	293	.0541	-2.56
81	.0980	0.69	Opened circuit		
91	.0986	0.20	296	.0564	-2.13
93	. . .	0.00	300	.0586	-2.08
98	.1302	-0.31 Reversed			

close enough together, as it is quite evident in the curve of Figure 7, which was drawn from another run at the same temperature.

9. Two criteria have long been considered most pertinent as describing the condition of a storage cell. One of these is the density of the electrolyte, and if care has been taken to keep this density right, it is possible to judge accurately of the condition of the cell by an examination of the electrolyte at a given point in the cell cycle. Usually the density is measured at full charge. It could as well be measured at the end of discharge or at any other known point in the cycle, provided the curves describing the relation between density and voltage

for a given current and at constant temperature were accurately known.

The other criterion of the condition of the cell now in use is the plate potential. In order that this may give useful information it is necessary to have a discharge curve, on which are plotted the cell voltages at various times of discharge at constant current and constant temperature. Once in possession of such a curve, measurement of

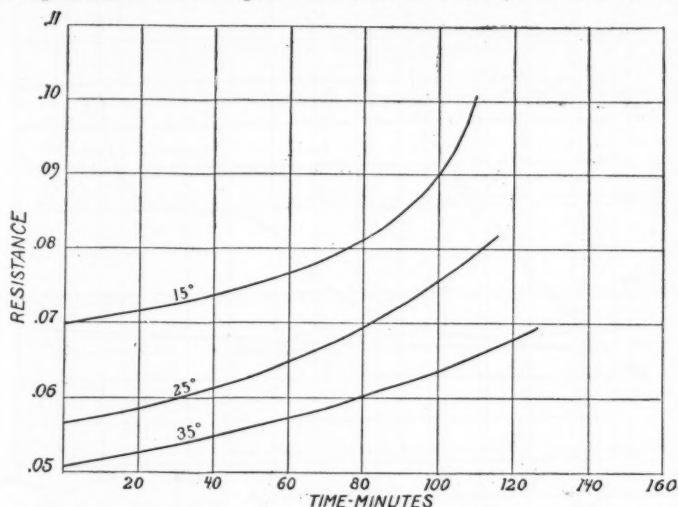


FIGURE 8. Curves showing resistance of paste plate cell during discharge at various temperatures.

cell voltage, at a known time after discharge at constant rate has begun, gives accurate information as to the condition of the cell.

It is evident that a measurement of the cell resistance serves equally well to determine the condition of the cell, for the resistance-time curves of Figure 5 are equally as characteristic as the voltage-time curves of Figure 6. The greater difficulty of measurement of cell resistance will probably prevent any practical application of this fact.

REVERSAL OF A PLANTÉ CELL.

10. It was considered a matter of interest to follow a cell at one temperature through complete discharge and then on to more or less complete reversal. If the explanation given on page 591 is correct, it

was to be expected that the resistance would decrease very rapidly after passing through a maximum near the end of complete discharge of the cell, and that the e. m. f. would also reverse rapidly and soon attain nearly its maximum with sign opposite the normal direction in the cell. Table VI. and Figure 7 show how well this is realized:

The data of the above table is plotted in the curves of Figure 7, and

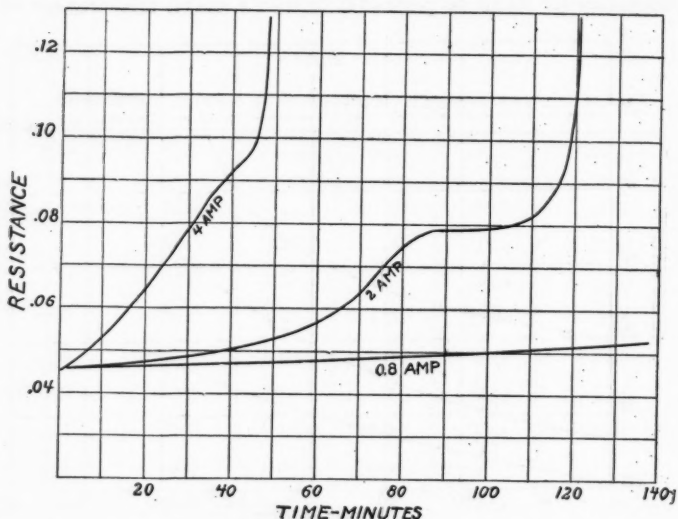


FIGURE 9. Resistance of Planté plate cell at various discharge rates.

they indicate qualitatively but clearly the course of the changes in the cell. It should be mentioned that the sharp point at the maximum of resistance (about .20 ohm) is only a rough approximation, as it was quite impossible to follow the change in this portion of the curve rapidly enough to insure accuracy. It is, however, quite certain that the point given is lower than the true maximum value.

PASTED PLATES.

11. New pasted plates were thoroughly charged and put through several cycles until their capacity was approximately constant. They were then set up in a cell with separation of the plates as nearly as possible that of the Planté cells. The curves given in Figure 8 show the course of the resistance during discharge at 2 amperes at various

temperatures. The points of special interest to be noted are the higher resistance of the cell and the smoothness of the curves. These pasted plates were made to have as nearly as possible the same capacity as the Planté cell at the 2-ampere discharge rate.

12. The course of the resistance of our Planté cell at constant temperature, but at various rates of discharge, is clearly shown by the

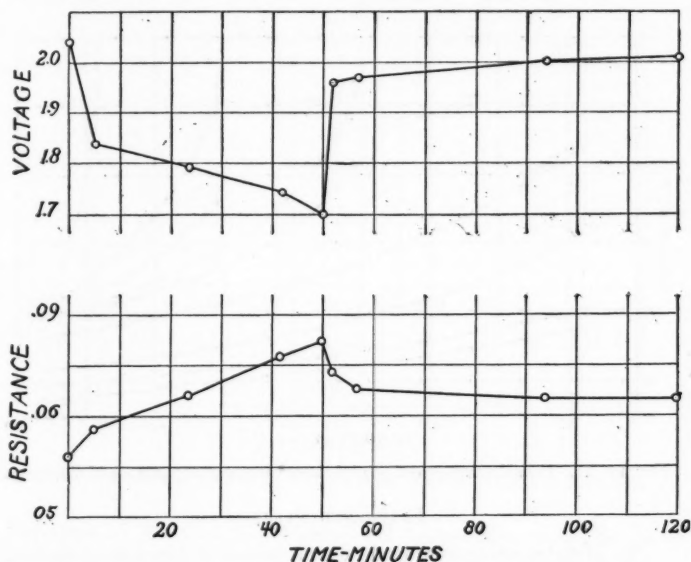


FIGURE 10. Voltage and resistance during partial discharge followed by recovery.

curves of Figure 9. It should be noted that these curves could be used as criteria of cell condition quite as well as voltage curves — and that the cell capacities corresponding to the different rates are clearly given by a statement of the cell resistance, corresponding to the rate in question, at which discharge must be stopped.

RECOVERY.

13. Curves showing resistance and voltage during partial discharge and subsequent recovery on open circuit are given in Figure 10. These curves are characteristic of the general shape of all recovery curves.

OVERCHARGE.

14. The resistance during overcharge seems to be a most variable factor. It rises and falls a thousandth of an ohm or so in one cell but has no regular course.

The disturbing factor must be the escaping gases as there is no other action going on in the cell.

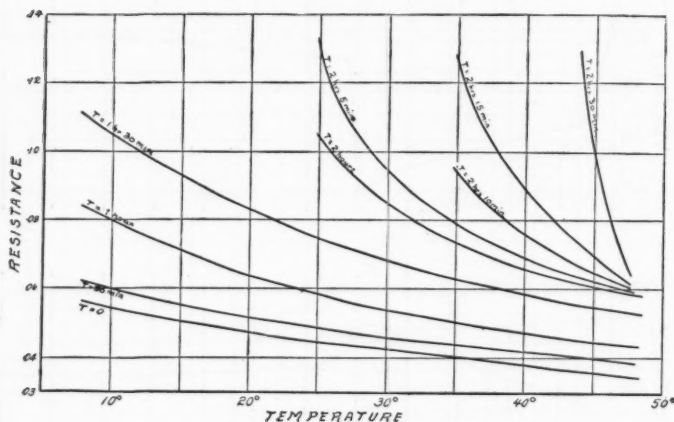


FIGURE 11. Temperature effect on resistance*after various periods of discharge.

SULPHATED PLATE.

15. Measurements were made over a period of a month or more on a nearly discharged plate. It showed no characteristic course whatever but varied from day to day over a range of several thousandths of an ohm, rising slightly during the first three weeks and then falling again. We evidently did not arrive at a sulphated condition in the usual understanding of the word.

THE TEMPERATURE-EFFECT ON RESISTANCE.

16. The curves of Figure 5 show the course of change of resistance during discharge at constant rate and constant temperature. They are isothermals. From these it is possible to construct *isochronal* curves of resistance *vs.* temperature, the isochronal curve corresponding to the fact that the same total amount of active material has been effected in each case, but at a different temperature. These curves are of special

interest because they show how *dynamic* a thing the momentary equilibrium in such a cell must be. A set of these derived curves is given in Figure 11. The points on the curve $T = 0$ are for open circuit and they give the temperature-resistance curve of Figure 4. The points on the curve $T = 30$ are resistances taken from the isothermal curves as they are cut by a vertical line at 30 minutes of discharge, and so on for the other curves.

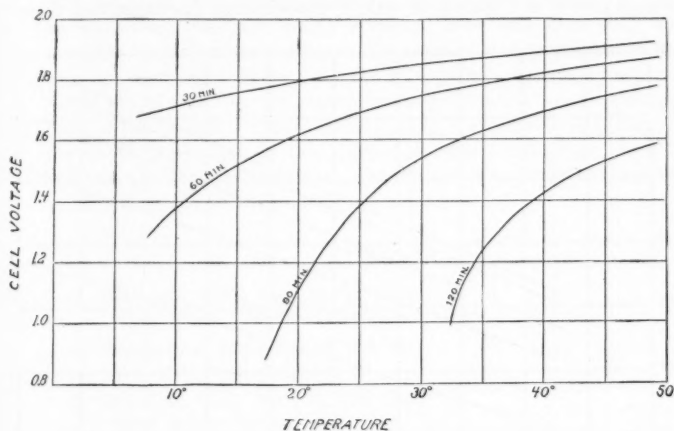


FIGURE 12. Temperature effect on voltage after various periods of discharge.

The slope of the line $T = 0$ gives the temperature-coefficient of resistance at the temperature corresponding to the point where the slope is determined. The slope at any point on one of the other curves is the temperature coefficient corresponding to the temperature where the slope is taken, but for all the curves except $T = 0$ the condition of the cell is one of dynamic momentary equilibrium. The slopes are nevertheless temperature coefficients corresponding to this particular state in the cell and they are of great interest in disclosing the condition of the cell. In fact it would be hard to find a more striking expression of the complex system under observation than that given by these curves.

The change in temperature-effect is enormous. At $T = 0$ the coefficient is about 1.5% per degree C. At $T = 150$ minutes the coefficient has reached 23% per degree C

THE TEMPERATURE EFFECT ON CELL VOLTAGE.

17. It must also be true that the isochronal lines of temperature and cell voltage will show a somewhat similar course. For while the resistance is a more complicated function of cell condition than the e. m. f. both factors must be largely determined by diffusion if final analysis were possible. Sections have been made of the isothermal voltage curves of Figure 6 at various times during discharge, and these

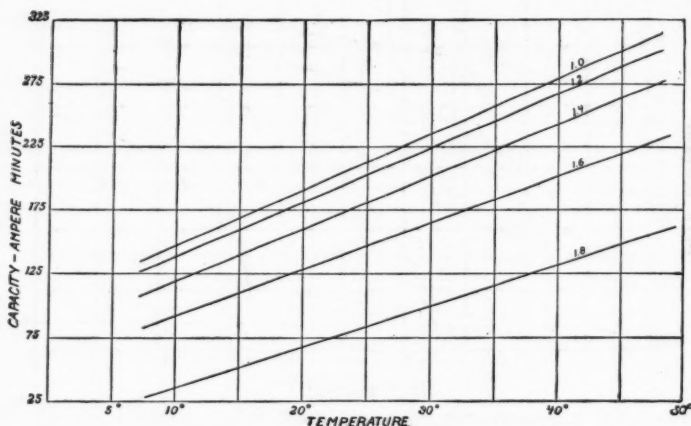


FIGURE 13. Temperature effect on capacity. Planté plates. One hour rate of discharge.

are plotted in the curves of Figure 12. No attempt has been made to determine the e.m.f. of the fully charged cell at various temperatures.

At 35° C. the coefficient of a cell which has been under discharge for 30 minutes is about 0.006 volts per degree, while that of a cell which has been running at the same rate for two hours is 0.62 volts per degree. [The open circuit temperature coefficient for this acid concentration is about .0003 volts per degree (Dolazalek).]

It should be kept in mind in considering this and the results indicated by the curves of Figure 11, that the cell contains throughout the course of each of the curves, exactly the same amount of each of its constituents. The same quantity of electricity has passed through it, and equal amounts of lead, lead peroxide and lead sulphate are present. The total amount of acid in the whole bulk of the

electrolyte is also the same in each case. The only difference is in the distribution of the materials in the cell.

TEMPERATURE COEFFICIENT OF CAPACITY.

18. From the data of these measurements it is also possible to calculate the temperature coefficient of the capacity of this type of plate. The values so obtained are plotted in the curves of Figure 13. It will be seen that they are nearly straight lines, and that they remain straight for various end voltages. In practice such plates would hardly ever be discharged below 1.6 volts at this rate, and the temperature coefficient of capacity, for plates discharged to this point, is about 3.5 percent per degree. This coefficient is only applicable to plates of this particular type, and to this discharge rate. For other plate types and various rates the temperature coefficient of capacity has been found to vary from 1.5 to 3.5 percent per degree.

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